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# ADSORPTION BEHAVIOR OF ORGANIC COMPOUNDS

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ABSTRACT

An adsorption theory of organic compounds is presented which is primarily based on data obtained for a mercury electrode by measuring the σ, ϕ- and C, ϕ-curves. It is found that adsorption on mercury of the majority of organic compounds reducing the double layer capacitance conforms to the isotherm equation of Frumkin.

Among the different direct and indirect methods for studying the adsorption of organic substances on electrode surfaces, the methods which measure the boundary stress (σ) and the differential capacitance (C) as a function of the electrode potential (ϕ) have been employed most extensively. The overwhelming majority of these data have been obtained for the boundary of a mercury/water solution with the small addition of organic compounds. In this connection, the adsorption theory of organic compounds which is presented below, is primarily based on experimental data obtained for a mercury electrode by measuring the σ, ϕ- and C, ϕ-curves. /1764*

Commencing with the studies by Gouy (Ref. 1, 2) and Frumkin (Ref. 3, 4), the method which measures the electrocapillary curves has been widely employed

* Note: Numbers in the margin indicate pagination in the original foreign text.

up to the present to study adsorption on a mercury electrode of different organic compounds (Ref. 5 - 20).

As may be seen from Figure 1, which was taken from the article by Gouy (Ref. 1), the adsorption of an organic compound (in this case, amyl alcohol) considerably decreases the mercury boundary stress. The maximum decrease in $\sigma$ occurs close to the zero charge point (zcp) in an inorganic electrolyte solution, and decreases with an increase in the negative or positive charge of the surface. In the majority of cases, no decrease in the boundary stress is observed when an organic substance is added, if there is an adequate negative, or positive charge, and the electrocapillary curve with the addition coincides with the $\sigma$, $\phi$-curve measured in a background solution (Figure 1). According to the adsorption equation of Gibbs, we have

$$d\sigma = -RT\Gamma \, d \ln c \tag{1}$$

where $\Gamma$ and c are the adsorption and concentration of the organic substance. This means that for large surface charges desorbtion of organic molecules from the electrode surface occurs. Qualitatively, this phenomenon is related to the replacement of the layer of organic molecules having a small dielectric constant by the layer of water molecules, in which the dielectric constant is much larger.

Figure 2 shows the $\sigma$, $\phi$-curves measured by Smirnov and Demchuk (Ref. 21) in a 0.2 M aqueous solution of NaI with 0.1 M addition of $n\text{-}C_5H_{11}OH$ over a wide potential range up to a charge of $Na^+$ ions which is accompanied by the formation of sodium amalgam. In the opinion of the authors, the divergence of the electrocapillary curves at very negative potentials has the same nature as that close to the mercury zcp, and is related to the adsorption of amyl alcohol close to the sodium amalgam zcp.

Frumkin (Ref. 22) has developed a quantitative theory for the influence of the electric field on the adsorption of neutral molecules. According to Frumkin, when allowance is made for the attractive force between ad- /1765 sorbed molecules, the decrease in the boundary stress ($\Delta\sigma$) and the extent to which the surface is covered ($\theta = \Gamma/\Gamma_\infty$) by an organic substance are related by the following relationship:

$$\Delta\sigma = -A\,[\ln(1-\theta) + a\theta^2] \qquad (2)$$

where A and $a$ are constants, and $A = RT\Gamma_\infty$. The quantity $a$ is a measure of the interaction between adsorbed particles (attraction constant).

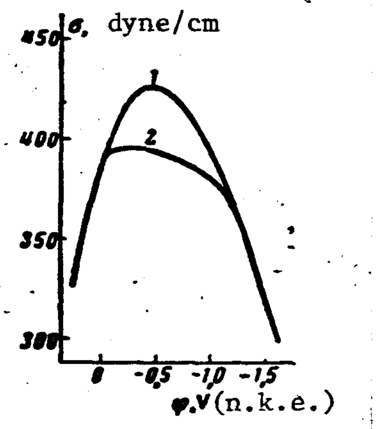


Figure 1

Electrocapillary Curves in the Following Solutions: 1- 1N $Na_2SO_4$; 2- 1N $Na_2SO_4$ + 0.1 M $C_5H_{11}OH$

(According to Data in [Ref. 1])

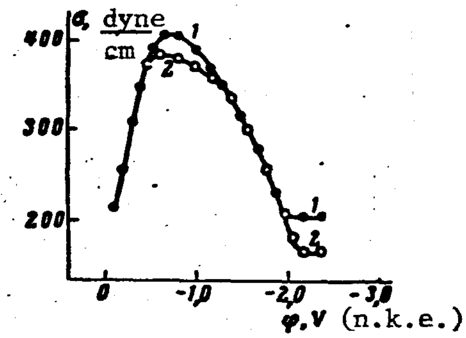


Figure 2

Electrocapillary Curves in the Following Solutions: 1- 0.2 M NaI; 2- 0.2 M NaI + 0.1 M n-$C_5H_{11}OH$

(According to Data in [Ref. 21])

We may readily obtain the equation of the adsorption isotherm from equation (2) and Gibbs' equation (1):

$$Bc = \frac{\theta}{1-\theta}\exp(-2a\theta) \qquad (3)$$

where B is the adsorption equilibrium constant which determines the dependence of adsorption on the electrode potential. Equation (3) has been called the

Frumkin isotherm.

In order to determine the explicit dependence of B on $\phi$, Frumkin assumed that the boundary between the electrode and the solution may be regarded as two capacitors connected in parallel; there are only molecules of an organic substance between the plates of one of the capacitors, and there are only solvent molecules (water) between the plates of the other capacitor. In this case, the electrode charge ($\varepsilon$) may be represented as follows:

$$\varepsilon = \varepsilon_0 (1 - \theta) + C'\theta(\varphi - \varphi_N) \tag{4}$$

where $\varepsilon_0 = \int_0^{\phi} C_0 d\phi$; $C_0$ and $C'$ - the capacitance of a double layer, respectively, in the case of $\theta = 0$ and $\theta = 1$; $\phi$ - the potential computed from the zcp in the case of $\theta = 0$ and $\phi_N$ - the zcp shift during the transition from $\theta = 0$ to $\theta = 1$.

When equation (4) is combined with the main electrocapillarity equation /1766

$$d\sigma = -\varepsilon d\varphi - RT\Gamma d\ln c \tag{5}$$

it leads to the following dependence of B on the potential:

$$B = B_0 \exp\left[-\frac{E + C'\varphi\left(\varphi_N - \frac{\varphi}{2}\right)}{A}\right] \tag{6}$$

where $E = \int_0^{\phi} \varepsilon_0 d\phi$, i.e., a decrease in $\sigma$ when there is adsorption of only inorganic ions.

The utilization of equations (6) and (3) makes it possible to compute the dependence of the coverage degree $\theta$ on the potential $\phi$. Based on equation (2), it is possible to find the decrease in the boundary stress under the influence of adsorption of organic molecules on the electrode surface.

Frumkin (Ref. 22) performed these computations for adsorption on mercury of tertiary $-C_5H_{11}OH$ of a 1 N solution of NaCl. He found that there was good agreement between the calculated $\sigma$, $\phi$-curves and those measured experimentally.

However, a more detailed comparison of the computational and experimental $\sigma$, $\phi$-curves in these experiments showed that the bend on the electrocapillary curves is more pronounced in the case of $\varepsilon > 0$ than would be expected from theory. This result was explained in (Ref. 22) by a decrease in the area of one adsorbed alcohol molecule with an increase in $\theta$, which is equivalent to the parabolic dependence on the potential of the attraction constant $a$.

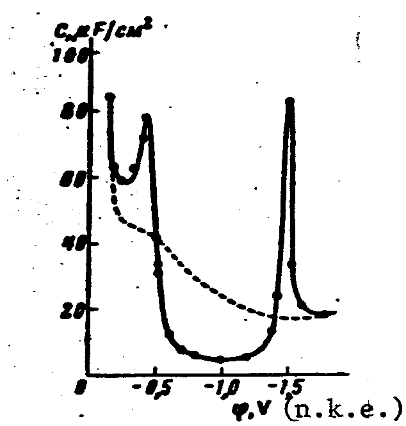


Figure 3

Curves Showing the Differential Capacitance in a 1 N Solution of $Na_2SO_4$ and in a 1 N Solution of $Na_2SO_4$ Saturated with $n-C_8H_{17}OH$ (According to Data in [Ref. 24]).

The theory advanced by Butler (Ref. 23) was an attempt to explain the electrocapillary curves on the basis of the molecular properties of adsorbed substances - in particular, taking into account the polarizability of organic molecules. However, in order to determine the dipole moments of adsorbed molecules, the theory advanced by Butler employed experimental data on boundary stress. In addition, this theory presented an incorrect dependence of the organic substance adsorption on its concentration in solution, since it was based on the validity of Henry's law.

Further development of the theory for adsorption of organic compounds may be based on experimental data derived from measuring the differential capacitance of a mercury electrode in the presence of organic additions, because the differential capacitance is a much more sensitive function of the change in the double layer structure than is boundary stress (Ref. 24). Based on the electrocapillary data and taking into account the Lippmann equation, we would expect a region of low capacitance (on the order of 4 - 5 $\mu F/cm^2$) on the curves showing the differential capacitance in the presence of organic substance additions. This region would be delineated on both sides by desorption peaks. In actuality, as was already shown by Proskurnin and Frumkin (Ref. 24), in the presence of n-octyl alcohol, the C, $\phi$-curves have the indicated form (Figure 3). A similar form for the capacitance curves was obtained subsequently by other researchers. /1767
Thus, commencing with the study by Proskurnin and Frumkin (Ref. 24), the method which measures the differential capacitance has been widely employed for studying adsorption on mercury of very different organic substances (Ref. 25 - 44).

However, the quantitative utilization of the data obtained is restricted to the region of maximum adsorption potentials, where there is a decrease in capacitance on the C, $\phi$-curve in the presence of organic substances (Figure 3), and where the following correct relationship holds between the capacitance and the degree of surface coverage:

$$C = C_0(1-\theta) + C'\theta \tag{7}$$

This equation was utilized in the studies (Ref. 34, 38, 42) in order to calculate the adsorption isotherms of different organic compounds on mercury. Dobren'kov recently employed the dependence of the capacitance on the coverage degree, in the case of a maximum adsorption potential, in order to develop an adsorption theory for two organic substances simultaneously on an electrode surface (Ref. 45, 46).

In order to interpret the complete curve of the differential capacitance in the presence of an organic substance, one must select an independent electric variable and a specific equation for the adsorption isotherm. The present discussion on these problems (Ref. 47 - 49) compels us to dwell on these problems in greater detail.

1. Selection of Electric Variable

When studying the adsorption of organic substances on electrodes, one may select either the electrode potential (Ref. 22) or its charge (Ref. 47) as the electric variable.

Let us first assume that the experimental dependence of an organic substance adsorption $\Gamma$ on its volumetric concentration and potential can be written as follows

$$Bc = f(\Gamma) \tag{8}$$

where B is a certain function of only $\phi$ and $f(\Gamma)$ - the function of only $\Gamma$. Under these conditions, it is advantageous to select the potential as the independent electric variable, since the form of the isotherm (8) will not depend on $\phi$ in dimensionless coordinates it follows from (8) that

$$\frac{d\ln B}{d\varphi} = -\left(\frac{\partial \ln c}{\partial \varphi}\right)_{\Gamma} = \frac{1}{RT}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_{\varphi} \tag{9}$$

where the second equation follows from the main electrocapillarity equation (5). Integrating (9), we find:

$$\varepsilon = RT\left(\frac{d\ln B}{d\varphi}\right)\Gamma + \varepsilon_0 = A\left(\frac{d\ln B}{d\varphi}\right)\theta + \varepsilon_0 \tag{10}$$

where, just as previously, $A = RT\Gamma_\infty$.

In the case of $\theta = 1$ and a given potential, let us designate the charge by $\varepsilon'$, and we then have

$$\varepsilon' = A\left(\frac{d\ln B}{d\varphi}\right) + \varepsilon_0 \tag{11}$$

It follows from equations (10) and (11) that

$$\varepsilon = \varepsilon_0(1-\theta) + \varepsilon'\theta \tag{12}$$

Differentiating equation (12) with respect to the potential for /1768 $\theta$ = const, we obtain equation (7). Thus, writing the adsorption isotherm in the form of equation (8) and, consequently, selecting the electrode potential as the independent electric variable, correspond to the model of a double electric layer which was previously advanced by Frumkin (Ref. 22).

If it is assumed as the first approximation that the capacitance $C_0$ does not depend on $\phi$, then it is apparent that $\varepsilon_0 = C_0\phi$, and we obtain the following from equation (4) in the case of $\varepsilon = 0$:

$$\varphi_{\varepsilon=0} = \frac{\varphi_N\theta}{\frac{C_0}{C'}(1-\theta)+\theta} \tag{13}$$

where $\phi_{\varepsilon = 0}$ is the zcp value for given $\theta$, calculated from the zcp in the case of $\theta = 0$ - i.e., the adsorption potential jump. As may be seen from equation (13), the dependence of $\phi_{\varepsilon = 0}$ on $\theta$ (or on $\Gamma$) is not linear when the potential is selected as the electric variable, and the larger the $C_0/C'$ ratio the greater it deviates from a linear dependence.

Let us now assume that the experimental data can be described by the following type of equation

$$Gc = f(\Gamma) \tag{14}$$

where G is a certain function only of $\varepsilon$ and $f(\Gamma)$ - the function only of $\Gamma$. In this case, it is advantageous to select the electrode charge as the independent electric variable, since the form of the isotherm (14) in dimensionless coordinates will not depend on $\varepsilon$. It follows from equation (14) that

$$\frac{d \ln G}{d\varepsilon} = -\left(\frac{\partial \ln c}{\partial \varepsilon}\right)_{\Gamma} = -\frac{1}{RT}\left(\frac{\partial \varphi}{\partial \Gamma}\right)_{\varepsilon} \tag{15}$$

where the second equation follows from the main electrocapillarity equation written in the case of $\varepsilon$ = const (Ref. 50). Integrating (15), we obtain

$$\varphi = -RT\left(\frac{d \ln G}{d\varepsilon}\right)\Gamma + \varphi_0 = -A\left(\frac{d \ln G}{d\varepsilon}\right)\theta + \varphi_0 \tag{16}$$

where $\phi_0$ is the value of $\phi$ in the case of $\theta = 0$, corresponding to the given charge $\varepsilon$.

In the case of given $\varepsilon$ and $\theta = 1$, if we designate the potential by $\phi'$, we then have

$$\varphi' = -A\left(\frac{d \ln G}{d\varepsilon}\right) + \varphi_0 \tag{17}$$

It follows from equations (16) and (17) that

$$\varphi = \varphi_0(1-\theta) + \varphi'\theta \tag{18}$$

Differentiating (18) with respect to $\varepsilon$ in the case of $\theta$ = const, we obtain

$$\frac{1}{C} = \frac{1-\theta}{C_0} + \frac{\theta}{C'} \tag{19}$$

Thus, writing the adsorption isotherm in the form of equation (14) and, consequently, selecting the electrode charge as the independent electric variable correspond to the consecutive combination of two capacitors with the capacitances $C_0/(1 - \theta)$ and $C'/\theta$. It is difficult for us to advance a physical interpretation of this model.

On the other hand, if the capacitances $C_0$ and $C'$ do not depend on $\varepsilon$,/1769 then it is apparent that $\phi_0 = \varepsilon/C_0$ and $\phi' = \varepsilon/C' + \phi$. In this case, equation (18) may be rewritten in the following form:

$$\varepsilon = \frac{\varphi - \theta\varphi_N}{\frac{1-\theta}{C_0} + \frac{\theta}{C'}} \tag{20}$$

Assuming that $\varepsilon = 0$ in equation (20), we obtain the linear dependence of the adsorption potential jump on $\theta$ ( or on $\Gamma$ ):

$$\varphi_{\varepsilon=0} = \theta\varphi_N \tag{21}$$

Thus, the dependence of adsorption potential jumps on $\Gamma$ enables us to determine whether condition (8) or (14) is more advantageous, and consequently, which of the electric variables ($\phi$ or $\varepsilon$) is more advantageous, when studying the adsorption of an organic substance at the phase boundary.

Figure 4 shows the dependence of $\phi_{\varepsilon = 0}$ on $\Gamma$ in the case of n-$C_4H_9COOH$ and n-$C_5H_{11}NH_2$ adsorption at the mercury-solution and solution-air boundaries (Ref. 51). As may be seen from Figure 4, the relationship between $\phi_{\varepsilon = 0}$ and $\Gamma$ at the mercury-solution boundary is independent of the background concentration and closely coincides with equation (13). However, it deviates sharply from the rectilinear dependence predicted by equation (21). At the same time, this dependence approximately follows equation (21) at the solution-

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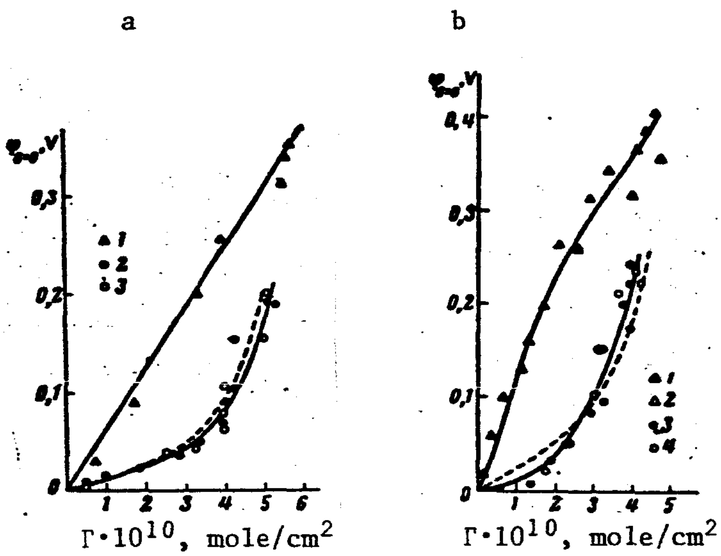


Figure 4.

**Dependence of** Adsorption Potential Jump on Adsorption of Organic Substance: a - Adsorption of n-$C_4H_9COOH$: 1- At the Solution-Air Boundary, 0.01 N $H_2SO_4$; 2 and 3- At the Mercury-Solution Boundary (2- 0.01 N $H_2SO_4$ Background; 3- 1 N $Na_2SO_4$ + 0.01 N $H_2SO_4$ Background); Dashed Line - Computed According to Equation (13) in the Case of $\phi_N = 0.2$ V, $\Gamma_\infty = 5 \cdot 10^{-10}$ M/cm$^2$ and $C_0/C' = 5$. b- Adsorption of n-$C_5H_{11}NH_2$; 1 and 2- On the Solution-Air Boundary (1- 0.05 N KOH Background; 2- 1N $Na_2SO_4$ + 0.05 N KOH Background); 3 and 4- At the Boundary of the Mercury-Solution (3- 0.05 N KOH Background; 4- 1 N $Na_2SO_4$ + 0.05 N KOH Background); Dashed Line - Computed According to Equation (13) in the Case of $\phi_N = 0.4$ V, $\Gamma_\infty = 5 \cdot 10^{-10}$ M/cm$^2$ and $C_0/C' = 5$.

air boundary*. We obtained similar results also in the case of adsorption at both n-$C_3H_7OH$ and n-$C_4H_9OH$ boundaries. /1770

It follows from the results obtained that, when studying the adsorption of organic compounds at the mercury-solution boundary, the electrode potential must be selected, and not its charge, as the electric variable, based both on a physical interpretation of the double layer

* Certain deviations of the dependence $\phi_{\varepsilon = 0} - \Gamma$ from a rectilinear dependence in the case of the solution-air boundary may be related to a change in the orientation of the adsorbed molecules with an increase in $\Gamma$.

model, and based on the experimental dependence of the adsorption potential jumps on the magnitude of the adsorption.

## 2. Selection of Adsorption Isotherm

Since the experimental isotherms for the adsorption of organic compounds may have both the form of a logarithmic curve, as well as a characteristic S-shaped form (Figure 5), when the equation of the adsorbed isotherm is selected it is only meaningful to examine those equations which can convey different forms of the experimental isotherms as a function of a certain value of $a$ (attraction constant). The following equations of adsorbed isotherms satisfy this condition:

1) the Frumkin isotherm - equation (3);

2) De Bur isotherm (Ref. 52):

$$Bc = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta}\right)\exp(-2a\theta) \tag{22}$$

3) Parsons isotherm (Ref. 47):

$$Bc = \frac{\theta}{1-\theta}\exp\left[\frac{2-\theta}{(1-\theta)^2}\right]\exp(\pm 2a\theta) \tag{23}$$

4) generalized equation of the Frumkin isotherm:

$$Bc = \frac{\theta}{(1-\theta)^n}\exp(-2a\theta) \tag{24}$$

obtained by the author (Ref. 53), which takes into account both the interaction between adsorbed molecules of an organic substance (by the quantity $a$) and the displacement of n solvent molecules (water) by one adsorbed particle.

In addition to the theoretical basis for one or another type of adsorption isotherm equation (Ref. 47, 48), criteria having an experimental nature

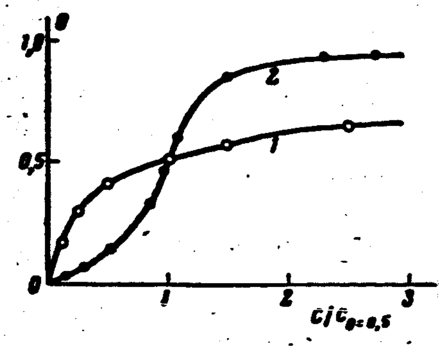


Figure 5

Adsorption Isotherms on Mercury:

1- Triethyl Ammonium Cations;

2- Tertiary Amyl Alcohol (According to Data in [Ref. 42, 43]).

are of decisive importance. Such criteria were advanced by Parsons (Ref. 47) and Tedopadze (Ref. 54). However, as was shown in (Ref. 55), they do not enable us to choose between the four equations of adsorbed isotherms which we have advanced. In this connection, let us investigate criteria which make it possible to perform this selection.

As may be readily seen, all the equations we have described have the following form:

$$Bc = F(\theta)\exp(-2a\theta) \tag{25}$$

where F(θ) is a certain function of θ which is independent of $a$. Taking /1771 the logarithm of (25) and then differentiating with respect to θ in the case of $\phi$ = const, we obtain

$$\left(\frac{\partial \ln c}{\partial \theta}\right)_{\phi} = \frac{d \ln F(\theta)}{d\theta} - 2a \tag{26}$$

As the analysis shows, for a certain value of $\Theta = \theta^*$, determined from the condition

$$\frac{d^2 \ln F(\theta)}{d\theta^2} = 0 \tag{27}$$

the dependence of $(\partial \ln c/\partial\theta)_\phi$ on $\theta$ passes through a minimum, whose position is caused only by the function $F(\theta)$, and does not depend on the attraction constant $a$.

As was shown in (Ref. 55), the values of $\theta^*$ for equations (3), (22), (23) and (24) are, respectively: 0.500; 0.333; 0.215 and $1/(1 + \sqrt{n}$. Thus, the position of the minimum on the experimental curves showing the dependence of $(\partial \ln c/\partial\theta)_\phi$ on $\theta$ may serve as a convenient criterion in selecting one of the four described isotherms. When this method is employed, only the equation of De Bur (22) is practically indistinguishable from equation (24) in the case of $n = 4$.

In order to obtain the experimental curves of the dependence $(\partial \ln c/\partial\theta)_\phi$, the procedure is as follows. First, employing the capacitance value at the minimum of the C, $\phi$-curves, with the aid of equation (7) which is valid, as we have seen, for any isotherm such as (8) or (25), we may compile the adsorption isotherm $\theta$ - c. Since $\frac{d \ln c}{d\theta} = \frac{dc}{c \cdot d\theta}$, the quantities $(\partial \ln c/\partial\theta)_\phi$ may be found according to the slope of this isotherm for different $\theta$, and the $(\partial \ln c/\partial\theta) - \theta$ curve may be compiled.

The characteristic curves obtained for the case of adsorption of analine, normal amylamine, and tertiary amyl alcohol on a mercury electrode, are shown in Figure 6. As may be seen from Figure 6, the minimum on these curves corresponds to $\theta^* \approx 0.5$, and consequently, adsorption of these compounds conforms to the Frumkin isotherm (3). Analogous curves showing the dependence of $\left(\frac{\partial \ln c}{\partial\theta}\right)_\phi$ on $\theta$ were also obtained for normal propyl alcohol, normal and iso-amyl alcohols, isoamylamine, cations of tetrabulammonia and phenol. The experimental values of $\theta^*$ range between 0.45 and 0.55 for all of these compounds (Ref. 55).

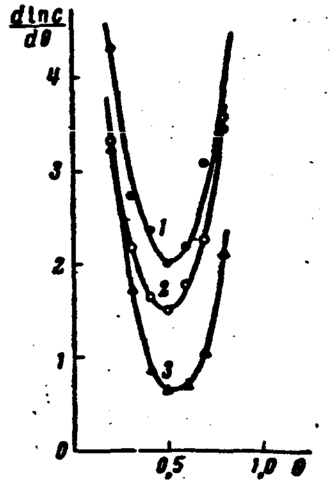


Figure 6

Dependence of $(\partial \ln c/\partial\theta)_\phi$ on $\theta$, Obtained from the Experimental Adsorption Isotherms:

1- Analine; 2- n-$C_5H_{11}NH_2$; 3- Tertiary $C_5H_{11}OH$.

Thus, adsorption on mercury of the majority of organic compounds reducing the double layer capacitance conforms to the isotherm equation of Frumkin (3). Dobren'kov and Golovin (Ref. 56) have recently shown that adsorption of dibutylsulfonnaphthaline and isoamyl alcohol on a cadmium electrode also complies with this equation*. Therefore, the isotherm equation of Frumkin (3) /1772

* The close agreement between equation (3) and the experimental data indicates that in the more general equation (24) n = 1, and, consequently, a group of several water molecules occupies one adsorption location on the electrode surface (Ref. 53). When allowance is made for the significant attractive force between the $H_2O$ molecules adsorbed on mercury (Ref. 57 - 59), this result can be explained by the fact that the work required to transfer this group of molecules, taken as a whole, from the surface into the volume will be less than the total work required to transfer each molecule separately.

may be preferably employed as the basis for a theory of differential capacitance curves in the presence of organic substances.

### 3. Quantitative Theory of Differential Capacitance Curves with the Addition of Organic Substances

The fact that the experimental data indicate that it is more advantageous to select the electrode potential as the electric variable, and to select the Frumkin equation (3) as the adsorption isotherm, compels us to reject the theoretical relationships advanced in (Ref. 42, 43, 47). This also compels us to reject the theory of Devanathan (Ref. 60) and Bockris, Devanthan, and Müller (Ref. 61), particularly due to the fact that the last two theories have several significant drawbacks which were investigated in detail in (Ref. 62).

If the potential is selected as the independent electric variable, under the condition that the adsorption of an organic substance on the electrode surface is not complicated by the formation of polylayers or micellar films, the surface charge is a function of only the electrode potential and the degree of coverage:

$$\varepsilon = \varepsilon(\varphi, \theta) \tag{28}$$

Thus, the general expression for the differential capacitance can be written as follows

$$C = \frac{d\varepsilon}{d\varphi} = \left(\frac{\partial\varepsilon}{\partial\varphi}\right)_\theta + \left(\frac{\partial\varepsilon}{\partial\theta}\right)_\varphi \cdot \frac{d\theta}{d\varphi} \tag{29}$$

The quantities $\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_\theta$ and $\left(\frac{\partial\varepsilon}{\partial\theta}\right)_\varphi$ in this equation can be immediately found from equation (4):

$$\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_\theta = C_0(1-\theta) + C'\theta \tag{30}$$

$$\left(\frac{\partial\varepsilon}{\partial\theta}\right)_\varphi = -[\varepsilon_0 + C'(\varphi_N - \varphi)] \tag{31}$$

In order to determine the derivative $d\theta/d\phi$, let us employ the isotherm equation (3). Taking the logarithm of this equation, and then differentiating with respect to $\phi$, after algebraic transformations we obtain

$$\frac{d\theta}{d\varphi}=\frac{d\ln B}{d\varphi}\cdot\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \tag{32}$$

It follows from equation (6) that

$$\frac{d\ln B}{d\varphi}=-\frac{\varepsilon_0+C'(\varphi_N-\varphi)}{A} \tag{33}$$

and therefore /1773

$$\frac{d\theta}{d\varphi}=-\frac{\varepsilon_0+C'(\varphi_N-\varphi)}{A}\cdot\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \tag{34}$$

Substituting the values of the derivatives from equations (30), (31), and (34) in equation (29), we obtain the final expression for the differential capacitance when there is an organic substance:

$$C=C_0(1-\theta)+C'\theta+\frac{[\varepsilon_0+C'(\varphi_N-\varphi)]^2}{A}\cdot\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \tag{35}$$

This equation was first obtained in the study by Hansen and his coworkers (Ref. 28).

As has already been indicated above, the utilization of equations (3) and (6) makes it possible to compute the dependence of $\theta$ on $\phi$ for a given organic substance concentration. Knowing this dependence, for the known constants $C'$, A, $a$ and $\phi_N$, we may employ equation (35) to calculate the total curve for the differential capacitance in the presence of an organic substance.

The computations performed by Hansen and his coworkers (Ref. 28), as well as our computations (Ref. 63), show that - in spite of the qualitative agreement between the computed and experimental C, $\phi$-curves - there is quite a quantitative divergence between them. As an analysis has shown, this divergence points to a change with the potential of the attraction constant included in the isotherm equation of Frumkin (3). In contrast to the assumption advanced by Frumkin (Ref. 22), for the majority of organic compounds, there is a linear dependence of $a$ on $\phi$, and not a parabolic dependence.

Thus, the development of a theory on the assumption of any arbitrary dependence $a = a(\phi)$ is of great interest.

In this case, taking the logarithm of equation (3) with subsequent differentiation with respect to the potential yields the following, after algebraic transformations, instead of equation (32):

$$\frac{d\theta}{d\varphi} = \left(\frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}\right)\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \qquad (36)$$

At the same time, differentiation with respect to $\phi$ in the case of $\theta$ = const yields:

$$\left(\frac{\partial \ln c}{\partial\varphi}\right)_{\theta} = -\left(\frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}\right) \qquad (37)$$

Taking into account the second equality in equation (9), we obtain

$$\frac{1}{A}\left(\frac{\partial\varepsilon}{\partial\theta}\right)_{\varphi} = \frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi} \qquad (38)$$

Integrating this equation and taking the fact into account that the integration constant equals $\varepsilon_0$, we obtain

$$\varepsilon = \varepsilon_0 + A\frac{d\ln B}{d\varphi}\theta + A\theta^2\frac{da}{d\varphi} \qquad (39)$$

Since $\varepsilon = \varepsilon' = C'(\phi - \phi_N)$ in the case of $\theta = 1$, we have the following from equation (39)

$$\frac{d\ln B}{d\varphi}=-\frac{\varepsilon_0+C'(\varphi_N-\varphi)}{A}-\frac{da}{a\varphi} \quad (40)$$

Integration of this equation from 0 to $\phi$ with subsequent involution /1774 yields

$$B=B_0\exp\left[-\frac{E+C'\varphi\left(\varphi_N-\frac{\varphi}{2}\right)}{A}\right]\exp(a_0-a) \quad (41)$$

where $a_0$ is the value of $a$ in the case of $\phi = 0$.

Equation (41) reflects the dependence of the adsorption equilibrium constant on the potential in the case of any arbitrary dependence of $a$ on $\phi$. As may be readily seen, in the case of $a$ = const it changes into equation (6).

Substituting equation (40) in (39), we obtain the equation for the electrode charge in the general case, when $a = a(\phi)$:

$$\varepsilon=\varepsilon_0(1-\theta)+C'\theta(\varphi-\varphi_N)-A\frac{da}{d\varphi}\theta(1-\theta) \quad (42)$$

As would be expected, equation (42) changes into equation (4) in the case of $a$ = const.

Finally, let us find the general expression for the differential capacitance in the presence of an organic substance under the condition $a = a(\phi)$. It follows from equation (42) that

$$\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_\theta=C_0(1-\theta)+C'\theta-A\frac{d^2a}{d\varphi^2}\theta(1-\theta) \quad (43)$$

$$\left(\frac{\partial\varepsilon}{\partial\theta}\right)_\varphi=-\varepsilon_0+C'(\varphi-\varphi_N)-A\frac{da}{d\varphi}(1-2\theta) \quad (44)$$

Substituting equation (40) in (36), we find

$$\frac{d\theta}{d\varphi}=-\left[\varepsilon_0-C'(\varphi-\varphi_N)+A\frac{da}{d\varphi}(1-2\theta)\right]\frac{1}{A}\cdot\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \quad (45)$$

Substituting the derivatives from equations (43), (44) and (45) in equation (29), we obtain the final expression for the differential capacitance:

$$C = C_0(1-\theta) + C'\theta - A\frac{d^2a}{d\varphi^2}\theta(1-\theta) + \frac{1}{A}\left[\varepsilon_0 + C'(\varphi_N - \varphi) + A\frac{da}{d\varphi}(1-2\theta)\right]^2 \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (46)$$

In the case of $a$ = const, equation (46) changes into the corresponding equation (35).

We previously obtained the expressions for the adsorption equilibrium constant B, the electrode charge $\varepsilon$, and the differential capacitance C, under the condition that the attraction constant is a linear function of the electrode potential:

$$a = a_0 + \beta\varphi \quad (47)$$

Allowance is made for the dependence of $a$ on $\phi$ in the expressions for B, $\varepsilon$ and C by introducing a certain new constant:

$$\varphi_N^0 = \varphi_N + \frac{\beta A}{C'} \quad (48)$$

The expressions (41), (42) and (46) obtained in this study have /1775 no restrictions imposed by condition (47), and are valid for any arbitrary dependence of the attraction constant on the electrode potential.

Since the observed dependence of the attraction constant on the potential for the majority of compounds studied, satisfies condition (47), the formulas obtained in (Ref. 64) provide a good agreement between the computed and experimental C, $\phi$-curves (Ref. 63, 65 - 68). Figure 7 illustrates this result with an example of adsorption on mercury of a normal valeric acid (Ref. 68). We also observed good agreement between calculations and experiments in the case of adsorption on mercury of n-$C_3H_7OH$; n-$C_4H_9OH$; n-$C_5H_{11}OH$;

$i-C_5H_{11}OH$; tertiary- $-C_5H_{11}OH$; $n-C_4H_9NH_2$; $n-C_5H_{11}NH_2$; $i-C_5H_{11}NH_2$; and $C_2H_5 - CO - C_2H_5$.

In the case of analine (Ref. 69) and also pyridine (Ref. 70) adsorption on mercury, the computed and experimental C, $\phi$-curves coincide only in the region of negative surface charges (see Figure 8). Due to $\pi$-electron interaction between analine or pyridine molecules having positive charges on the surface of mercury, with the change from $\varepsilon < 0$ to $\varepsilon > 0$ their reorientation occurs, which is accompanied by partial desorbtion. The anode maxima on the C, $\phi$-curves in the presence of analine or pyridine contribute to this process, and not to the total desorbtion of organic substance molecules from the electrode surface. It is clear that under these conditions for $\varepsilon > 0$ the theoretical C, $\phi$-curves, which do not take into account the indicated anomalies in the adsorption of an organic substance, cannot present the pattern of the experimental curves for differential capacitance.

Finally, in the case of adsorption of phenol on mercury (Ref. 71) the planar distribution of molecules, which is related to the strong $\pi$-electron interaction, is characteristic for all of the potential regions of its adsorption. In this case, the constants included in the equation for B(41) and for the differential capacitance (46) characterize the planar configuration of phenol molecules in an adsorbed state, so that the computed and experimental C, $\phi$-curves coincide in the entire potential region (Figure 9). However, the influence of $\pi$-electron interaction is manifested in the fact that the agreement between calculations and experiments is much worse in the case of phenol than it is in the case of adsorption of aliphatic compounds (see Figure 7).

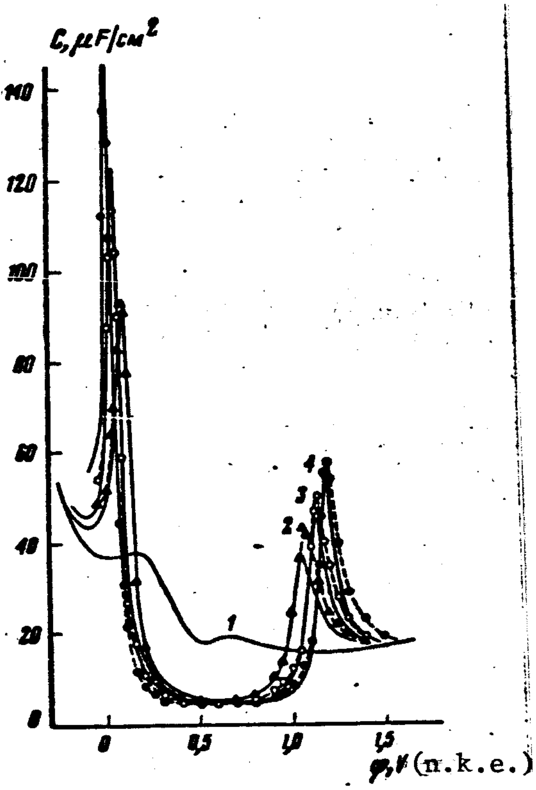


Figure 7.

Curves for Differential Capacitance in a 0.05 N Solution of $Na_2SO_4$ with Additions of n-$C_4H_9COOH$ in the Following Concentrations

1- 0; 2- 0.05; 3- 0.08 and 4- 0.12 M.

The Solid Lines - Experimental Data for 400cps; Dots and Dashes - Calculations.

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In addition to a quantitative interpretation of the curves for differential capacitance in the presence of an organic substance, equations (3), (41) and (46) enable us to study certain general patterns of equilibrium (i.e., extrapolated to a zero frequency) and also non-equilibrium C, $\phi$-curves - particularly, the dependence of the peak potentials on the C, $\phi$-curves and the heighth of these peaks on the organic substance concentration. A study of

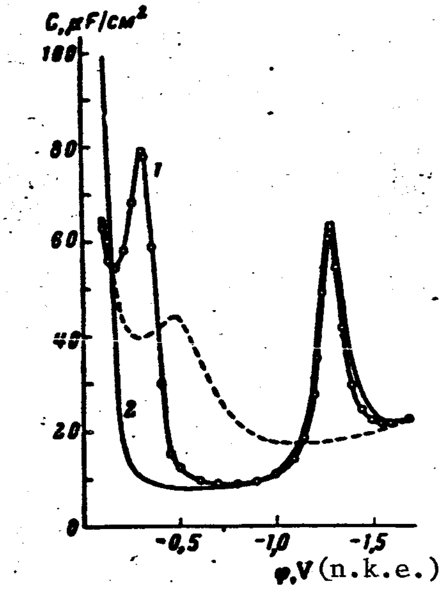


Figure 8.

Curves for the Differential Capacitance in a 0.1 N Solution of KCl (Dashed Line) and with the 0.1 M Addition of Analine:

1- Experimental Data; 2- Computed Curve.

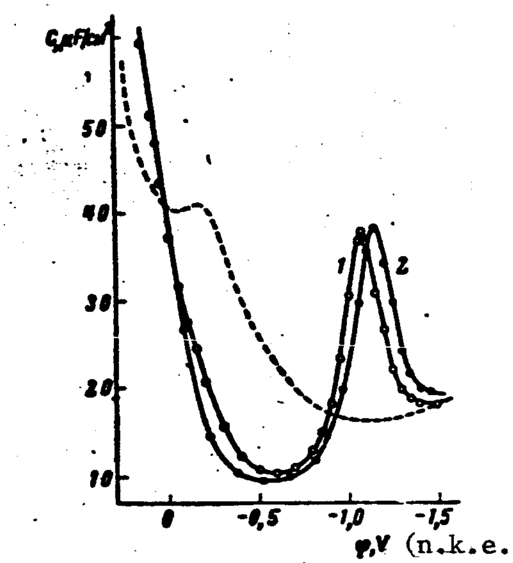


Figure 9.

Curves for the Differential Capacitance in a 1 N Solution of $Na_2SO_4$ (Dashed Line) and with a 0.05 M Addition of Phenol:

1- Experimental Data; 2- Computational Curve.

these dependences is of great importance, since they make it possible to develop methods for determining the main constants included in equations (41) and (46), as well as the dependence of $a$ on $\phi$ according to experimental curves for the differential capacitance. Damaskin and Tedoradze (Ref. 72 - 76) have recently studied the problems connected with establishing those general patterns which are of independent scientific interest.

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